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Natural waters in Amazonia

III. Ammonium Molybdate-Reactive Silica

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Introduction

Most silica in water is probably derived from the decomposition or metamorphism of silicate minerals rather than from solution of quartz, as quartz is one of the rock minerals most resistant to attack by water (U.S. Geol. Surv., 1958). Detailed information on the structure and chemical composition of silicate minerals is given by HÜCKEL (1950) and MASON (1952). These papers may aid in understanding the decomposition processes of rocks and their relation to natural water composition, although the mechanisms of the breakdown of silicates are not fully understood yet.

Analytical procedures

- 1) apparatus — spectrophotometer PMQ II/ZEISS.
- 2) reagents — a) $(\text{NH}_4)_6 \text{Mo}_7 \text{O}_{24} \cdot 4 \text{H}_2\text{O}$ (5 g) + 5 ml H_2SO_4 conc. (diluted to 100 ml)
b) Oxalic acid (10%)
c) SnCl_2 (3 g) + 50 ml HCl conc. (diluted to 250 ml)
- 3) procedure

To 5 ml sample

- add 1 ml (2a), mix, wait about 10 minutes
- add 1 ml (2b), mix, wait about 5 minutes
- add 1 ml (2c), mix, determine silica content of the sample and the blank (distilled water + reagents).
- Read using an 0/850 μm filter, amplifier.

Interferences

Pyrex bottles were used for collection and storage of water samples. No contamination of samples was observed. The water remained in contact with the glass a short time only and all samples had a low pH. For silica determination the condition were such that phosphates, hydrogen sulfide, ferric and ferrous iron did not interfere with the analytical procedure.

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In the Amazonian Tertiary region under study (Fig. 1) the degree to which silicate is taken into solution may be affected by many factors. These include rock decomposition rates, the mineral constituents of the red or white sandstone layers, the podzolic or podzol soil complexes, the yellow to yellow-red latosols, such climatic agents as temperature and rainfall and, last but not least, by the silica units present.

The general scientific concept and the description of sampling sites (Fig. 1) are given by BRINKMANN (in press).

Results

The ammonium molybdate-reactive silica content of all natural waters collected in the Tertiary region along the Manaus-Itacoatiara Road during 1969 was computed as dry season (June—October), wet season (November to May) and yearly average (Table 1).

The qualitative model given in BRINKMANN (in press) was applied to determine the ammonium molybdate-reactive silica compounds in the hydrological cycle of high tropical rain forest sites and clearcut areas of the Amazonian Tertiary formations. The Rio Negro water represents approximately the soluble silica "steady state system" of the region (Table 1 — V 4).

Input

Dry season, wet season and yearly soluble silica averages of all input fractions [rainfall (I); stemflow (II), etc. in Table 1] are low but irregular, showing a dependence on site specific differences in stand composition and stem overgrowth patterns.

1) No soluble silica was recorded for rainwater averages (Table 1). Some silica traces in samples may occur, when samples show the effect of local meteorological events, such as wind spouts. Thermal imbalance and subsequent wash-out or dry fallout on the clearcut spots may be assumed as the source.

2) Soluble silica content in stemflow (Table 1) appears irregular, but considerably higher at sampling site II—2. Silica leaching at the bases of epiphytes and bromeliads may be the main source, although decomposition of organic matter in the canopy region may contribute to some extent also.

3) The seasonal and yearly averages of soluble silica content in throughfall (II 1—5) are irregular and low. Leaf and branch leaching and additional aerosol wash-out in the canopies may be the main sources. Variations may be influenced by site exposure to the main wind direction and the different silica content in plant material of each stand.

"Delta storage"

The seasonal and yearly soluble silica content of ground waters (IV 1—3) is significantly uniform, but site specific in concentration. Although wells IV—1 and IV—2 are sunk into quartz-sand layers, the silica concentration is quite low. Relatively high percolation and ground water flow rates reduce silica availability to a minimum, because of short-term contact. In addition, under acid conditions the silica seems to be relatively immobile and easy to aggregate. Well IV—3, however, shows concentrations at least double those

given above. The higher concentrations of soluble silica may be the result of complex flow and solution dynamics. The water body is in contact with river water, ground water and rainwater, thus providing a long-term exposure to quartz sands. Humic acids and carbon dioxide may play a part also (BRINKMANN and SANTOS, in press).

Output

With the exception of Rio Negro water (V 4), three river waters (V 1—3) show seasonal and yearly soluble silica averages similar to the groundwater of well IV—3. The soluble silica content during the year is quite uniform. About 80 percent of the Tertiary strip along the Manaus-Itacoatiara Road is covered with very heavy or heavy latosols. According to IPEAN (1969) the SiO_2 concentrations of these soils (ME/100 g T. E. S. A.) down to 1.50 m depth oscillate between 27 and 36 percent, but the hydrogen ion concentration (pH) is very high (3.8 pH to 4.9 pH.). Therefore, silica will be somewhat immobile and easily aggregated. According to KOBAYASHI (1960) water soluble silica is most abundant in river waters which drain igneous rocks and volcanic soil complexes. South-east Asia river waters show the highest "available" silica content in the Philippines (average of soluble silica in 8 rivers—30.4 mg/l) and Japan (average of soluble silica in 225 rivers — 19.0 mg/l). Taiwan and West Pakistan river waters, however, are much lower in available silica and may be compared, according to Livingstone (1963), with European (7.5 ml/l) and North American (13.1 mg/l) concentration patterns.

In addition, KOBAYASHI (1959) gives the averages of soluble silica in India (15 rivers—average 17.6 mg/l); Ceylon (7 rivers—average 13.1 mg/l); and Thailand (30 rivers—average 16.0 ml/l).

Conclusions

In general, soluble silica concentrations of natural waters of the Tertiary region studied are low, although silica in soils and rocks is quite high.

The input fraction (rainfall, stemflow and throughfall) shows either no silica present or very low concentrations. About 90 percent of all values are lower than 1.0 mg/l, while at about 80 percent are lower than 0.5 mg/l (Table 2). This may include some local, stand specific variations in soluble silica stemflow concentrations (Table 2—II 2).

The storage fraction (groundwater) shows soluble silica concentrations between 0.1 and 1.5 mg/l. Ninety percent of the total values are lower than 1.5 mg/l. An exception is shown under IV—3. Soluble silica content varies between 0.4 and 3.5 mg/l (Table 2). Various agents and complex flow dynamics are probably responsible.

Soluble silica concentrations of the high rain forest streams (V—1 to 3) of the output fraction are slightly higher than all other natural waters analyzed, excluding the Rio Negro water (V—4). About 90 percent of all values are lower than 2.0 mg/l (Table 2). In comparison to Philippine and Japan river waters, the soluble silica concentrations are extremely low and only confirm the results of numerous previous analyses of many amazonian waters of the corresponding geological area (cf. STOLI 1968). Siliceous sponges are abundant in the seasonally flooded rain forest strips (Igapó) along the Rio Negro banks and in the mouth areas of tributaries. These may have a small effect on cycling silicon, but up to now, the influence of these sponges is not clearly understood. The Rio Negro shows the highest concentrations, with more than 90 percent of all values between 2.0 mg/l and 3.0 mg/l soluble silica. Since the Rio Negro drains a watershed of about 650000 Km^2 , these concentrations may be assumed to be the soluble silica "steady state" system of the region.

Summary

Natural waters of the Amazonian Tertiary formations along the Manaus-Itacoatiara Road were studied with respect to variations in average seasonal and yearly soluble silica content. In general the variations are small and concentrations very low, for all input fractions, i. e., rainfall, stemflow, and throughfall [about 90 percent of the total (470 analyses) lower than 1.0 mg/l]. While 90 percent of total ground water analyses (excluding well IV 3) have soluble silica concentrations lower than 1.5 mg/l, high rain forest stream waters are slightly higher (90 percent of all values lower than 2.0 mg/l). The Rio Negro waters show 90 percent of the total samples analyzed between 2.0 mg/l and 3.0 mg/l soluble silica.

Table 1. Yearly and seasonal soluble silica averages of natural waters in Amazonia. — Total 470 analyses.

Soluble Silica (mg/l)														
Rain-fall	Stemflow		Throughfall					Ground Waters			River & Stream Waters			
I	II ₁	II ₂	III ₁	III ₂	III ₃	III ₄	III ₅	IV ₁	IV ₂	IV ₃	V ₁	V ₂	V ₃	V ₄
0.1	0.5	0.8	0.2	0.1	0.1	0.7	0.4	0.9	0.9	2.0	1.9	1.7	2.2	2.7
0.0	0.1	0.8	0.4	0.9	0.3	0.3	tr	1.9	0.9	1.9	1.8	1.7	1.9	2.7
0.0	0.3	0.8	0.2	0.4	0.2	0.5	0.4	0.9	0.9	1.9	1.9	1.7	2.0	2.7
														yearly averages

Table 2. Soluble silica relative frequency distribution in natural waters in Amazonia — Total 470 analyses.

Frequency (Percent)															
Range SiO ₂ (sol.) mg/l	Rain- fall	Stemflow		Throughfall					Ground Waters			River & Stream Waters			
	I	II ₁	II ₂	III ₁	III ₂	III ₃	III ₄	III ₅	IV ₁	IV ₂	IV ₃	V ₁	V ₂	V ₃	V ₄
0 —0.5	100.0	88.2	40.0	79.3	78.6	86.2	70.8	79.2	3.6	14.8	3.7	3.1	13.2	2.2	
0.5 ₁ —1.0		5.9	37.1	20.7	3.6	13.8	25.0	16.7	53.6	44.4	11.1	18.8	21.0	20.0	
1.0 ₁ —1.5		5.9	14.3		10.7		4.2		42.9	37.0	22.2	37.5	57.9	31.1	
1.5 ₁ —2.0			2.9					4.2		3.7	14.8	40.6	7.9	33.3	2.8
2.0 ₁ —2.5			2.9		7.1						25.9			11.1	22.2
2.5 ₁ —3.0			2.8								3.7			2.2	75.0
3.0 ₁ —3.5											14.8				

Resumo

Águas naturais da formação terciária da Amazônia na faixa da Estrada Manaus-Itacoatiara foram estudadas com relação às variações estacionais e anuais do conteúdo em sílica solúvel.

Em geral, as variações são pequenas e baixas nas suas concentrações. Isto é verdade para todas as frações entradas, como por exemplo água da chuva, água que escorre pelos troncos e água das copas — gotas —. Aproximadamente 90% do total das análises (470 amostras examinadas) têm valores abaixo de 1.0 mg/l. Na fração armazenada, em 90% do total (excusivo o pôto IV 3) a concentração é mais baixa que 1.5 mg/l. Nos igarapés da mata tropical os teóres são mais elevados, 90% do total estão abaixo de 2.0 mg/l. No Rio Negro, 90% do total estão entre 2.0—3.0 mg/l de sílica solúvel.

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